

New voltammetric sensors for alkaline cations based on ionophores incorporated into a self-assembled thiol monolayer

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In the last 30 years a huge number of different ionophores with high affinity and selectivity^{1,2} for various anionic and cationic species have been synthesized and developed in the field of ion-selective electrodes (ISEs). They are mainly used in organic liquid membranes³ to prepare and commercialize the well-known potentiometric sensors (ISEs) for a large number of analytes. They can be also incorporated into polymer matrices, used as coating for metal electrodes to prepare chemically modified electrodes (CMEs)⁴.

In this study, we developed a new type of reliable and selective voltammetric sensors based on ionophores embedded into thiol self-assembled monolayers (SAMs) on gold electrodes. The detection mechanism is that of ion-channel sensors (ICSs)⁵, which detect electrochemically an electroinactive analyte bound to the ionophore by controlling the rate of marker redox reaction. Embedding ionophores into the thiol SAMs can lead to ion-channel sensors of simple and rapid preparation.

Due to the increasing worldwide demand of reliable and rapid analytical techniques for the widest variety of analytes⁶ in various solvents and in presence of many other compounds, the development of a flexible and rapid characterization method of new ionophores is urgently needed. In this context, a major goal is the optimization of a stable fixed matrix in which the ionophore under study can be quickly introduced and removed to investigate its interactions with the primary and interfering ions in different solvents.

In the present work the preparation and characterization of Li⁺ and K⁺ responsive CMEs, based on commercial ionophores incorporated into SAMs, is presented and discussed. These electroinactive analytes were determined using three-electrode voltammetric measurements performed in aqueous solutions, with a marker as electroactive species. The cation is bound to the ionophore and controls the rate of marker redox reaction. The embedment process is largely controlled by the chemical affinity between the two molecules. To obtain long-life sensitive electrodes it is important to tune the molecular dimension of the selected ionophores with the chain length of alkanethiols provided that chemical incompatibilities between the organic moieties of thiols and ionophores are excluded. We tested several thiols with a different length of carbon chain and a different

terminal group.

The results are discussed in terms of interactions between ionophores and different length thiol chain.

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